UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF LITHIUM-BASED SOLID STATE BATTERY MATERIALS

MUHAMMAD AMIN IDREES

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PREPARATION AND CHARACTERIZATION OF LITHIUM-BASED SOLID STATE BATTERY MATERIALS

By

MUHAMMAD AMIN IDREES

Thesis Submitted in Fulfilment of the Requirements for the Degree of Doctor of Philosophy in the Institute of Advanced Technology Universiti Putra Malaysia

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

PREPARATION AND CHARACTERIZATION OF LITHIUM-BASED SOLID STATE BATTERY MATERIALS.

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August 2000

Chairman: **Associate Professor Mansor Hashim, Ph.D.**

Faculty: **Institute of Advanced Technology**

Three different cathodes such as $LiMn_2O_4$, $LiCoO_2$ and $Li_2Ni_8O_{10}$ were synthesized by the sol-gel technique The said materials at low temperature were achieved through the low temperature technique The X-ray diffraction study of the compounds confirmed the formation of single-phase compound at higher calcination temperature At low temperatures the X-ray diffractogram of the samples showed the presence of low intensity diffraction lines with weak impurities indicating the existence of crystallinity but these were not indexed to any kind of impurities of $LiMn_2O_4$ $LiCoO_2$ and $Li_2Ni_8O_{10}$ The formation temperatures of the compounds were analyzed using DTA The DTA studies showed clearly the lowest formation temperature and this formation temperature depends upon the gelating agent used in the present study The lowest formation temperatures recorded were 208 ^{0}C for $LiMn_2O_4$, 201 ^{0}C for $LiCoO_2$ and 214 ^{0}C for $Li_2Ni_8O_{10}$

The thermogravimetric analysis showed that the compounds were stable up to 800 ^{0}C The EDAX analysis was performed for the compounds to identify the purity of the compounds The EDAX spectrum showed that there was no impurity present in the compounds It ascertained the formation of single-phase compounds by XRD Because of low atomic weight lithium could not be detected other than that the EDAX showed the presence of the respective atoms The particle size distribution of the compounds showed that the particles were distributed in large volume The particle diameter increased with the increase of calcination temperature Grinding reduced the large volume distribution and the particle diameter After grinding by mortar and pestle hand grinder, the particle size was reduced much and the distribution was narrowed down, thereby the surface area of the particle was increased

The SEM analysis also confirmed the sub-micron size reduction and the distribution was narrowed down, thereby the surface area of the particle was increased The compounds were used as electrode materials for lithium ion batteries The battery analysis showed that the capacities of the $LiMn_2O_4$, $LiCoO_2$ and $Li_2Ni_8O_{10}$ were 10 mAh , 24 mAh and 5 mAh respectively

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENYEDIAAN DAN PENCIRIAN BAHAN-BAHAN BATERI KEADAN PEPEJAL LITIUM

Oleh

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Ogos 2000

Pengerurusi: **Profesor Madya Mansor Hashim, Ph.D.**

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Tiga jenis bahan katod iaitu $LiMn_2O_4$, Li CoO_2 dan $Li_2Ni_8O_{10}$ telah disintesis menggunakan kaedah itu 'sol-gel'. Kaedah suhu rendah ini menghasilkan bahan-bahan yang tersebut di atas pada suhu rendah. Kajian belauan sinar-X terhadap sebatian-sebatian ini mengesahkan pembentukan sebatian fasa tunggal pada suhu 'kalsinasi' yang lebih tinggi. Pada suhu rendah difraktogram sinar-X sampel-sampel menunjukkan kewujudan puncak-puncak belauan yang kecil beserta kehadiran sedikit bendasing, menandakan kewujudan sifat kehabluran, tetapi tidak pula merujuk kepada sebarang ketidaktulenan $LiMn_2O_4$ teroksida. Suhu pembentukan sebatian tersebut dianalisa menggunakan kajian DTA menunjukkan dengan jelas suhu pembentukan terendah ini dan suhu pembentukan ini bergantung kepada 'gelating agent' yang digunakan didalam penyelidikan ini. Suhu pembentukan terendah yang direkodkan adalah 208°C bagi $LiMn_2O_4$, 201°C bagi Li CoO_2 dan 214°C bagi $Li_2Ni_8O_{10}$.

Analisa termogravimetrik menunjukkan sebatian-sebatian tersebut adalah stabil sehingga 800°C. Analisa EDAX dilakukan untuk mengenalpasti ketulenan sebatian-sebatian tersebut. Spektrum EDAX menunjukkan tidak terdapat bendasing di dalam sebatian-sebatian tersebut. Fakta ini ditentusahkan lagi dengan kewujudan fasa tunggal seperti ditunjukkan oleh XRD. Disebabkan jisim atom litium yang rendah ia tidak dikesan, melainkan dengan menggunakan EDAX mengesahkan kehadiran atom-atom yang berkenaan. Taburan saiz zarah bagi sebatian-sebatian tersebut menunjukkan bahawa zarah-zarah berkenaan tersebar di dalam isipadu yang besar. Diameter zarah bertambah dengan pertambahan suhu 'kalsinas'. Proses licikan boleh mengurangkan taburan isipadu yang besar dan diameter zarah. Selepas licikan dilakukan dengan mortar dan "pestle hand grinder",saiz zarah menurun dengan ketara dan taburan isipadu dikurangkan.

SEM juga mengesahkan zarah-zarah tersebut adalah bersaiz sub-mikron. Sebatian-sebatian tersebut telah digunakan sebagai bahan katod bagi bateri litium-ion. Analisa ke atas bateri menunjukkan nilai kapasiti bagi $LiMn_2O_4$ adalah 10 mAh, bagi $LiCoO_2$ adalah 24 mAh dan bagi $Li_2Ni_8O_{10}$ adalah 5 mAh.

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"Verily never will Allah change the condition of peoples until they change it themselves (with their own souls)" - Al-Quran

Allah s.w.t blessed me throughout my life. The deepest glory and honor unto him. Without His help, I was unable to pursue and complete this impassable task of my doctoral research.

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I certify that an Examination Committee met on 18th August 2000 to conduct the final examination of Muhammad Amin Idrees on his Doctor of Philosophy thesis entitled "Preparation and Characterization of Lithium-Based Solid State Battery Materials" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been peviously or concurrently submitted for any other degree at UPM or other institutions.

MUHAMMAD AMIN IDREES

Date: 11-09-2000

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LIST OF SYMBOLS AND ABBREVIATIONS/NOTATION

Ah	ampere-hour
Ah/L	ampere-hours per liter
Å	angstrom
A	ampere
α	alpha
Ah	ampere-hour
Ah/kg	ampere-hours per kilogram
β	beta
Cm	centimeter
C	coulomb
Cr	chromium
Co	cobalt
Cl	chlorine
Cu	copper
$C_o(NO_3)_2$ $6H_2O$	cobaltous(II) nitrate hexahydrate
C_6 H_8 O_7 H_2 O	citric acid
$C_4H_6O_4$	succinic acid
CH (COOH) (OH) COOH	maleic acid
(CHOH COOH)$_2$	tartaric acid
DEC	diethyl Carbonate
DTA	differential thermal analysis
DMC	dimethyl carbonate

E_0	standard potential (in volts)
EC	ethylene Carbonate
EPDM	ethylene propylene dine monomer
F	faraday constant (96500 C or26 8 Ah)
Fe	iron
g	gram
ΔG	Gibbs free energy change
I	current
IR	Internal resistance of a cell
JCPDS	Standards, Joint Committee on Power Diffraction Standards, Index to the Powder Diffraction File, Swarthmore,Pa.
Kg	kilogram
Li-ion	lithium-ion
$LiNO_3$	lithium nitrate
Li_2CO_3	lithium carbonate
$Li_2Ni_8O_{10}$	lithium nickel oxide
$LiCoO_2$	lithium cobalt oxide
$LiMn_2O_4$	lithium manganese oxide
$LiClO_4$	lithium perchlorat
$LiMeS_2$	lithium transition metal sulphide
$LiMeS_{e2}$	lithium transition metal selenide
$LiMeO_2$	\lithium transition metal oxide
$LiMO_2$	lithium metal oxide

LiFeO2	lithium iron oxide
$LiBF_4$	lithium-tetrafluoroborat
$LiCF_3SO_3$	lithium trifluoromethane-sulfonate
$LiTi_2O_4$	lithium titanium oxide
LiV_2O_4	lithium vanadateoxide
$LiCoVO_4$	lithium cobalt vanadateoxide
$LiNiVO_4$	lithium nickel vanadateoxide
mAh	milli-ampere hour
m^2	square meter
m^3	cubic meter
M(mole)	amount of substance
Me	transition metal
mAh/g	milli-ampere hour per gram
Mn	manganese
Mo	molybdnum
MCFC	molten carbonate fuel cells
"n"	no of electrons involved in the electrochemical reaction
N	nitrogen
Ni	nickel
Ni-Cd	nickel cadmium
$Ni(NO_3)_2 . 6 H_2O$	nickel (II) nitrate hexahydrate
O	oxygen
PVDF	polyvinylidene fluoride